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## **INVENTION AND PATENT OFFICE**

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### **(54)    Procedure to produce trithiocarbonate compounds**

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(57) The invention relates to a procedure to produce trithiocarbonate compounds from carbon bisulphide and trithiocarbonate in the form of salts in solution. Trithiocarbonate compounds are important intermediary products for the production of pesticides and insecticides. It was found that solutions of hydroxides in water with carbon bisulphide could be converted into trithiocarbonate. The reaction can be accelerated by the use of phase transfer catalysts. The aqueous solutions of trithiocarbonate produced by this can be used to make other trithiocarbonate compounds.

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## **Procedure to produce trithiocarbonate compounds**

### **Scope of application of the invention**

The invention relates to a procedure to produce trithiocarbonate compounds from carbon bisulphide and trithiocarbonate in the form of salts in solution. Trithiocarbonate is an important preliminary stage for the production of 1,3-dithiol-2-thiones, tetrathiafulvalenes and other sulphur compounds. Trithiocarbonate and trithiocarbonate compounds are important intermediary products for the production of pesticides and insecticides or can themselves be components of such active substances. In addition, these compounds are sometimes effective against microorganisms like fungi and bacteria.

### **Characteristics of the known technical solutions**

Trithiocarbonate and its derivatives are already well known and have been characterised in detail (M.DRÄGER and G. GATTOW, *Angewandte Chemie*, 80, 22 [1968] page 954).

The syntheses that lead to trithiocarbonate and thereby to substituted trithiocarbonate compounds, are mostly based on a conversion of hydrogen sulphide with oxides or hydroxides, for example from alkali or earth metals in aqueous or alcoholic solutions, to sulphide and the subsequent conversion of carbon bisulphide to trithiocarbonate (*Organic Synthesis, Collection Volume IV*, page 967).

Alkali and earth trithiocarbonate can in this way be isolated in crystalline form on the basis of the available solubility. Trithiocarbonate can in solution with the usual alkylating or arylating agents be easily converted into the corresponding dialkyltrithiocarbonates or diaryltrithiocarbonates. Trithiocarbonate compounds, for example trithiocarbonate-diacetic acid, can also be produced by heating thiocarbonyl ethoxy thioglycolic acid with aqueous alkali (HOLMBERG, *Journal fuer praktische Chemie*, 71, 271 [1905] and BILMANN, *Justus von Liebig's Annalen der Chemie*, 348, 134 [1906]) or by conversion of potassium-methylxanthate with sodium monochloracetate.

In addition trithiocarbonate-diacetic acid can be maintained with sodium acetate if an aqueous solution of potassium-ethyl trithiocarbonate is heated.

In addition trithiocarbonate derives from the reduction of carbon bisulphide with alkali metals or by the electrical current in dimethylformamide or other polar, aprotic solution agents (G. STEIMECKE, H.J. STELER, R. KIRMSE, E. HOYER, *Phosphorous und Sulfur*, 1979, 7 [1], pages 49 to 55). The state of the art procedures are very complex.

### **Aim of the invention**

The aim of the invention is to produce trithiocarbonate and dialkyl, diaryl, dialkenyl, dialkynyltrithiocarbonate or cyclic trithiocarbonate simply without using carbonate bisulphide or sulphide.

### **Explanation of the nature of the invention**

The invention is intended to find a procedure to produce trithiocarbonate compounds from carbon bisulphide. It was a complete surprise to find that solutions of hydroxide in water with carbon bisulphide could be converted into trithiocarbonate. The temperature used for this reaches -20 to +100 °C, but is not restricted to this. The reaction can be accelerated by using trithiocarbonate solutions. The aqueous solutions of trithiocarbonate produced by this can be used to make other trithiocarbonate compounds. Hence general formula I can be produced by reactions with substances of general formula R-X trithiocarbonate compounds, whereby R alkyl, aryl, arakyl, cycloalkyl, alkenyl, alinyl and heterocyclic 1 to 4 residues signify nitrogen and/or oxygen or sulphur atoms, which if need be can be substituted one or more times. The residual R can, however, also produce one to four methyl groups, producing cyclic trithiocarbonate compounds. X means a leaving group, for example a halogen atom, a sulphonate, alkoxysulphate or a sulphate residue. The invention therefore consists in converting carbon bisulphide with hydroxides and subjecting the reaction product formed by this to alkylation or arylation. Dimethylsulphate can be produced with dimethyltrithiocarbonate and chloracetic acid with trithiocarbonate-diacetic acid.

The following examples should explain the invention in more detail:

### **Illustrative embodiments**

#### **Example 1**

A solution of 48g sodium hydroxide in approx. 400 ml water is mixed with 40 ml carbon bisulphide and heated under reflux conditions for 4 to 8 hours while being stirred. After evaporation of the unconverted carbon bisulphide into a vacuum, an aqueous solution is produced containing up to 0.4Mol trithiocarbonate and in this form is appropriate for conversion.

#### **Example 2**

40 ml of carbon bisulphide in a solution of 48g sodium hydroxide and 2 g triethylbenzylammonium chloride is placed in 500 ml water and heated for approx. 4 hours under reflux conditions. After the carbon bisulphide has largely been converted, it is cooled at approx. 40°C and a solution of 80 g chloracetic acid and 32 g sodium hydroxide is added dropwise, whereby the temperature of the reaction mixture rises while this is added. It is left to stand overnight and acidified with concentrated mineral acid at 0 to 5°C to pH 1. After being drained off and washed with cold water this produces 82 g raw product, F: 165.5 to 173°C. The recrystallisation from 3 volume parts of ethanol and 1 volume part water produces trithiocarbonate-diacetic acid.

Yellow crystal, F: 172 to 174°C

Acid no; 496; 498 calculated: 494

IR (KBr)  $\text{cm}^{-1}$ : 1350, 1052, 1650 (wide), 1210, 880, 1396, 2925 and 2970.

### **Example 3**

A potassium trithiocarbonate is produced from 76 g of 90% potassium hydroxide, 40 ml carbon bisulphide and 500 ml water.

Beginning at 20°C a solution of 87 g  $\beta$ -chlorpropionic acid and 32 g sodium hydroxide is added dropwise to 200 ml water for 10 minutes while being stirred, stirred for 3 seconds at 60°C and for another 1.5 seconds at 70°C.

After standing overnight it is acidified while being iced with mineral acid at pH 1, drained off, washed with water and receives 90 g of raw product. The recrystallisation from 2 volume parts of methanol and 1 volume part of water produces trithiocarbonate-di(3-propionic acid).

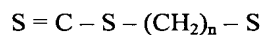
Yellow crystal, F: 108 to 110°C

Acid no: 437; 435 calculated: 442

IR (KBr)  $\text{cm}^{-1}$ : 2950 (wide), 1690 (COOH), 1425, 1400 1275, 1200, 1060, 820

**Claims:**

1. Procedure to produce trithiocarbonate compounds, **characterised in that** carbon bisulphide with hydroxides is converted into monovalent or bivalent cations in aqueous solution agents or aqueous solutions, the received trithiocarbonate reaction solutions are subjected to alkylation or arylation to compounds with the general formula  $IS = C(SR)_2$ , whereby  $R_2$  = monovalent or bivalent cations with the same or different alkyl, aryl, aralkyl, cycloalkyl, alkenyl, alkynyl and heterocyclic 1 to 4 residues signify nitrogen and/or oxygen or sulphur atoms, which if need be can be substituted one or more times by carboxyl, carboxylate, green acid, sulphonate, amidocarbonyl, halogen, amino, acyclamino, acyl, alkoxy, alkylthio and hydroxyl residue and the trithiocarbonate reaction solutions with compounds with the general formula  $X-(CH_2)_n - Y$  are converted into cyclic trithiocarbonates with the general formula II



Whereby X and Y represent leaving groups and amount to n1 to 4.

2. Procedure according to point 1, **characterised in that** the conversion of carbon bisulphide with hydroxides can also be done in the presence of phase transfer catalysts.  
In this regard 1 page formulas

